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(54) Title: DIE COATINGS FOR GRAVITY AND LOW PRESSURE DIE CASTING

(57) Abstract

A die coating for use on the surface of a metal mould or die component contacted by molten metal in low pressure or gravity die casting, said die coating including a porous layer of ceramic material produced by co–deposition, using a thermal spraying procedure, of a powder of said ceramic material and a powder of a suitable organic polymer material and, after the co–deposition, heating of said polymer material to cause its removal.

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DIE COATINGS FOR GRAVITY AND LOW PRESSURE DIE CASTING

Technical Field

This invention relates to die coatings, to a process for providing permanent mould or die components with an improved die coating, and to a die coating material for use in such process.

Background

In low pressure and gravity die casting, the surface of each metal mould or die component, which is contacted by molten metal, is provided with a mould or die coating. Under current procedures, a ceramic-based coating is used at a thickness of from about 0.05 to 1.0mm. The main function of the coating is to provide a degree of insulation which is intended to prevent premature solidification of the molten metal, and thereby enable the complete filling of the die cavity before solidification starts. However, the coating also is to protect the steel die surfaces from erosion or corrosion by impingement by or contact with molten metal.

Current die coating technology involves the use of a water-based suspension of ceramic particles containing a water-based binder, most commonly sodium silicate. Coating mixtures of this type need to be properly stored, while stirring and testing to prepare them for use often involves tedious procedures. The coating is applied to the sand or shot blasted surface of a die component using a pressurized air spray gun. For this, the component is preheated, typically from about 150 to 220°C, such that water is evaporated from the die surface, enabling the binder to polymerize and bond the ceramic particles together and to the die surface.

The die coatings produced with the current aqueous ceramic suspensions are highly porous. The level of porosity may range from about 30 to 60%, depending on the size and shape of the ceramic particles and the amount of binder used. High porosity gives the coating very good insulating properties. However, the strength of the coatings is limited by the strength of the binder used (about 6.9 MPa in the case of sodium silicate) and the level of porosity of the coating.

Important factors in a thermally insulating die coating are porosity and surface roughness. Also, wear resistance is important since a coating with an inadequate level of wear resistance is prone to damage in use, with a consequential reduction in its useful life-time. The sodium silicate bonded coatings, produced with the current aqueous ceramic suspensions, have a low level of wear resistance which results in them having a productive life-time of not more than about two to four 8-hour shifts. However, even during such a short life-time, production needs to be stopped from time to time to enable repair of the coating by a "touch-up" operation.

In US patent 4,269,903 to Clingman et al, there is disclosed a ceramic seal coating formed on at least one of two relatively rotatable members, such as rotating air foils of an axial flow compressor. The process seeks to provide a seal coating as disclosed in US patent 4,055,705 to Stecura et al, which has improved abradability. The coating of US 4,055,705 comprises a bond coat of NiCrAlY alloy applied to a substrate and a thermal barrier which is applied over the bond layer and comprises zirconia stabilized with another oxide. The advance provided by US 4,269,903 is in providing over that thermal barrier layer an abradable layer of porous stabilized zirconia. The porous layer is formed by thermal decomposition of organic filler material, which is co-deposited with stabilized zirconia onto the barrier layer. The co-deposition, such as by plasma spray or thermal spray process, preferably uses separate streams of organic and zirconia powders, with the organic powder chosen from a range of suitable thermoplastics. After co-deposition, the organic material is decomposed by heating, to leave an abradable zirconia layer having a porosity of from about 20 to about 33% and, hence, a suitable level of abradability. The abradable layer enables wear of at least one of two relatively rotatable components in rubbing contact such that loss of a fluid seal between the components is avoided.

In the process of US 4,269,903 the organic material is used because, after its co-deposition with zirconia, the organic material is able to be removed by thermal decomposition to leave a porous, and hence abradable, layer of zirconia. An alternative purpose for co-deposition of organic powders with ceramic and/or metal powders is disclosed in US patent 5,718,970 to Longo.

The process of US 5,718,970 is concerned with providing a substrate with a thermally sprayed duplex coating of a plastics material which is co-

deposited with a higher melting point ceramic material and/or metal. It is asserted that while metal and ceramic powders necessitate spraying with high temperature gas streams, such as plasma sprays or acetylene gas, plastic powders are usually sprayed with low temperature gas streams, such as hydrogen or natural gas, to prevent superheating and oxidation of the plastic powder. The solution for achieving a duplex coating is to use a powder comprising particles having a core of plastic material and, on the core, a substantially continuous particulate cladding of ceramic and/or metal. The cladding may be adhered to the core as a consequence of heating to soften the core, or by use of a suitable binder. The duplex coating produced by thermal spraying of such powders is able to exhibit characteristics of the ceramic and/or metal and of the polymer material, with the coating indicated as having particles of the plastic material dispersed in a continuous matrix of the ceramic and/or metal.

Disclosure of the Invention

The present invention seeks to provide an improved die coating, a process for providing a permanent mould or die component with a an improved die coating and a die coating material for use in the process of the invention.

An improved die coating according to the present invention, for use on the surface of a mould or die component contacted by molten metal in low pressure or gravity die casting, includes a porous layer of ceramic material produced by co-deposition, using a thermal spraying procedure, of a powder of the material and a powder of a suitable organic polymer material and, after the co-deposition, heating of the polymer material to cause its removal.

The invention also provides a process for providing a die coating on such surface of a metal mould or die component, wherein an initial coating of organic polymer material and ceramic material is formed on the surface by co-deposition of powders of the materials by a thermal spraying procedure, and the initial coating is heated so as to remove the polymer material and leave a porous coating of the ceramic material.

The polymer material may be heated so as to remove the polymer material by combustion and/or by decomposition, with decomposition generally being preferred.

The thermal spraying procedure used in the present invention may be of any suitable type. Thus the co-deposition may be by flame spraying, plasma spraying or electric arc spraying.

The die coating of the present invention and the process for its production have some features which seemingly are similar to features of the disclosure of US patent 4,269,903 in relation to a porous abradable layer. However, as indicated above, the disclosure of 4,269,903 is concerned with an abradable ceramic seal coating on at least one of a pair of members, which move relative to each other in rubbing contact. That is, the disclosure is quite unrelated to the context of a die coating for surfaces of metal mould or die components contacted by molten metal. Moreover, the disclosure of US patent 4,269,903 is limited to a porous layer of stabilized zirconia, which is abradable. In contrast, the die coating of the invention in addition to not being limited to the use of zirconia, has an enhanced level of wear resistance which enables a substantially increased useful life-time relative to current die coating technology discussed above. There is little basis for correlating abradable in the context of US 4,269,903 with wear resistance in the context of a die coating. However, particularly as a die coating is required to have a high level of abrasion resistance in order to be able to withstand the impingement and flow of molten metal at the high temperature levels prevailing in low pressure and gravity die casting, the benefits resulting from the die coating of the invention are surprising in view of the disclosure of US patent 4,269,903 which teaches an abradable, rather than an abrasion resistant, coating.

The ceramic powders which are used in providing the die coating of the present invention may be a processed powder conventionally used in the production of ceramic articles. Thus, the powder may be selected from at least one metal compound such as oxides, nitrides, carbides and borides. Suitable examples include alumina, titania, silica, stabilized zirconia, silicon nitride, boron nitride, silicon carbide, tungsten carbide, titanium borides and zirconium boride. However, the ceramic powder may be of a suitable mineral origin such as clay minerals, hard rock ore and heavy mineral sands such as those of ilmenite, rutile and/or zircon. One particularly suitable powder is that obtained from scoria or pumice, since powder particles of these materials are internally porous and have the added benefit of being of angular form.

A wide range of plastics and like materials can be used to provide the organic polymer powder. Important requirements for selection of these are availability in a suitable powder form and an ability to withstand sufficiently the temperatures to which they are exposed during thermal deposition. A further requirement is an ability to be combusted or decomposed at practical temperatures and in practical reaction times. In large part, the materials comprise thermoplastics, such as polystyrene, styrene-acrylonitrile, polymethacrylates, polyesters, polyamides, polyamide-imides and PTFE.

The respective powders, that is the ceramic powder and the polymer powder, preferably are of a relatively narrow size spectrum. In general, they preferably are of particle sizes not more than about 60 μm and not less than about 1 μm in the case of the ceramic and not less than about 5 μm in the case of the polymer material.

The process of the invention can be used in a variety of forms. In one form, a substantially uniform die coat is provided over all surfaces of mould or die components, which define a die cavity. The coating may, for example, have a thickness of from about 250 to 400 μm, such as from about 300 to about 400 μm. In that form, the coating provides insulation over all surfaces of the die cavity, enabling filling of the cavity before molten metal being cast commences solidification.

The die coating provided by the invention, because of its porosity, acts as a thermal barrier. In contrast, a non-porous coating of the same material will be less effective as a thermal barrier. This enables alternative useful forms of the invention in which use is made of a die coating according to the invention in combination with a non-porous coating. In one alternative, one surface or part of the overall surface defining a die cavity is provided with a non-porous ceramic die coating which is less insulating, while other surfaces or parts of the surface are provided with a thermal barrier die coating according to the invention. This arrangement enables heat energy extraction, from molten metal in the die cavity, to be at a higher rate through the non-porous coating than through the porous thermal barrier die coating. Thus, directional solidification is able to be facilitated, to achieve solidification of the molten metal in a direction away from the non-porous coating.

In a further alternative, all surfaces defining a die cavity, or one or a part of such a surface, can be provided with successive die coatings which alternately are porous and non-porous. That is, the full thickness of at least part of the die coating may consist of at least two layers of a sandwich or lamella form. As a consequence, the die coating will have a thermal conductivity intermediate that of corresponding coating thickness of non-porous and porous die coatings, respectively, of the same ceramic material. Thus, the range of differential control over heat energy extraction from molten metal being cast can be enhanced.

In each of those alternatives of the invention, the porous and non-porous regions or layers of the die coating may be of the same ceramic material or of a respective ceramic material.

In order that the invention may more readily be understood, the description now is directed to the following Examples.

Example 1

Ceramic powder and polymer powder were mixed and subjected to flame spraying to form a co-deposited coating on a die cavity defining the surface of a low pressure metal die cast component. The ceramic powder was Metco 210 grade zirconia stabilized by 24% magnesium oxide for which the data sheet indicated a particle size range of (-53) to (+10) μm, a melting point 2140°C and a density of $4.2 gcm^{-3}$. The polymer powder was of polystyrene supplied by Huntsman Chemical Company Australia Pty. Ltd., which had been ground to -45μm under liquid nitrogen, using a SPEX Freezer mill. The powder mixture of $MgO(24\%)ZrO_2$/polystyrene contained 15 volume percent (4wt%) of polystyrene.

The co-deposition of the powder mixture was performed using a Metco Type 6P-II Thermospray system, with a P7C-K nozzle and a 3 MPa powder feeder, under the following conditions:

Pressure:	oxygen $2.07x\ 10^{-1}$MPa; acetylene $1.035x10^{-1}$ MPa;
Flow:	oxygen 20 l/min; acetylene 24 l/min m^3S^{-1}
Carrier Gas:	N_2 at 3.78 $x10^{-1}$ MPa and 18 l/min
Powder Feeder:	15 (rpm)
Spray Distance:	76 mm

Also, the system used an air jet, which operated at a pressure of $3.45x10^{-1}$ MPa and crossed at 63.5 mm from the nozzle.

Following co-deposition of the blended powders, the deposited coating was heated to 450°C for one hour to cause the polystyrene to decompose. Polystyrene decomposes fully at 320 to 350°C in nitrogen (DTA/TGA). The porous, stabilized zirconia coating resulting from removal of the polystyrene by decomposition was found to comprise an excellent die coating in having good abrasion resistance enabling it to withstand the impingement of molten metal during low pressure and gravity die casting. The die coating also exhibited a low heat transfer coefficient, such that solidification of molten metal during such casting was able to be delayed until filling of the die cavity was complete.

Example 2

The overall procedure of Example 1 was repeated, with scoria powder used instead of stabilized zirconia. The scoria powder was produced by drying scoria rocks in an oven at 100°C, crushing the dried rocks using a ring mill, and sieving the crushed rock using a shaker and several screens of decreasing size to separate the powder. The scoria powder used had a size range of 45 to 75 μm and a density of 2.9gcm^{-3}. It was blended with polystyrene powder, as produced and characterized in Example 1, to achieve a blend having 15 volume percent of polystyrene.

The conditions of flame spraying and decomposition of the co-deposited polystyrene were as detailed in Example 1. The resultant porous, scoria die coating was of similar characteristics to the zirconia coating produced in Example 1, but was more effective as a thermal barrier coating due to it having a lower heat transfer co-efficient than zirconia.

Example 3

Three powder blends with 15 vol% polystyrene were produced in the manner detailed in Example 1. Each of these differed from Example 1 in that the size range of the polystyrene powder blended with the MgO (24%) stabilized ZrO_2 was 45 to 75 μm, 75 to 106 μm and 106 to 150 μm, respectively.

In contrast to Example 1, each of the three powder blends was co-deposited by plasma-spraying, using a spray gun designated as a SG100 subsonic having a power rating of 40 kw, an anode setting of 185 volts, a cathode setting of 129 volts and a gas injector, Miller 113. Operating parameters used were:

Power:	open circuit 160V, operating power at 33V and 800A
Arc/Primary gas:	argon, critical orifice No. 56 (flow rate 47 l/min), pressure reg. 3.45 x10^{-1} MPa
Auxiliary/Secondary gas:	helium, critical orifice No. 80 (flow rate 12 l/min), pressure reg. 3.45 x 10^{-1} MPa

Powder gas/carrier:	argon, critical orifice No. 77 (6 l/min), pressure reg. 2.76 x 10^{-1} MPa, hopper 2.8 rpm
Spray distance:	96 mm

Following co-deposition of each of the three powder blends, the deposited coating was heated as detailed in Example 1. The porous, stabilised zirconia coatings resulting from the removal of polystyrene by decomposition were of similar characteristics to the coating produced in Example 1.

Example 4

The overall procedure of Example 3 was repeated, using a blend of scoria powder produced as in Example 2 and -45 μm polystyrene powder produced as in Example 1. The condition of plasma spraying of the scoria/15 vol% polystyrene powder blend, and decomposition of co-deposited polystyrene, was the same as in Example 3. The resultant porous scoria die coating was of similar characteristics to that produced in Example 2.

The process of die coating using the current technology is considered as an art in which the control of coating quality and thickness are highly operator dependent. The bond between ceramic particles provided by polymerized sodium silicate is not very strong. Therefore, sodium silicate bonded coatings are fragile and not wear resistant.

On the other hand, in the new die coating system of the present invention, there is no separate binder. The ceramic particles are partially melted and then bonded together which provides stronger bonding system. Changing the percentage of the porosity of the coating can alter the heat transfer coefficient properties of the die coating of the present invention. This can be easily achieved by changing the percentage of the polymer used in producing the die coating. This gives the advantage to tailor directional solidification for the die casting part to minimize the occurrence of shrinkage related defects.

Use of the present invention is very flexible. Changing the polymer size can change the surface roughness of the coating. For the purpose of good adhesion a first layer of the coating can be applied without addition of polymer.

A second layer can contain polymer particles to provide porosity to improve insulating properties of the coating. A final layer can be also without polymer if very smooth surface is required.

Low pressure and gravity die casting processes require that the molten metal flow readily in the complicated die cavity in order to create the die casting. Low pressure die casting in particular involves the movement of molten metal against gravity in order to fill the die cavity completely. Often the molten metal is transported through narrow sections and the insulation provided by the die coating is found to be critical in these areas. The surface roughness of the coating affects the ability of the molten metal to flow into the die cavity by creating minute pockets of air between the peaks of the coating and where it contacts the molten metal. The molten metal does not completely wet the total surface area of the coating, and these pockets of air are an important factor influencing fluidity and therefore the filling of the die cavity in order to produce sound castings.

The addition of evaporable components, specifically polymer powders creates a high degree of porosity as well as affecting the surface profile of the resultant coating. This surface roughness can be changed by changing the size of the polymer particles added to the ceramic powder mix for plasma sprayed coatings. The flexibility of changing the surface roughness also has applications in influencing the surface finish of the final casting.

The variation in surface roughness with polymer particle size can be illustrated with reference to Example 3. A die coating produced with the MgO(24%) stabilized ZrO_2 of that Example, without added polymer, was found to have a surface roughness of R_a of 4.5μm. The die coating produced using the zirconia and 15 vol% of 45 to 75 μm polystyrene had a surface roughness R_a of 10 μm, while that produced with 15 vol% of 75 to 106μm polystyrene had a surface roughness of 25μm.

Finally, it is to be understood that various alterations, modifications and/or additions may be introduced into the constructions and arrangements of parts previously described without departing from the spirit or ambit of the invention.

CLAIMS:

1. A die coating for use on the surface of a mould or die component contacted by molten metal in low pressure or gravity die casting, said die coating including a porous layer of ceramic material produced by co-deposition, using a thermal spraying procedure, of a powder of said ceramic material and a powder of a suitable organic polymer material and, after the co-deposition, heating of said polymer material to cause its removal.

2. A die coating according to claim 1, said ceramic powder being selected from at least one metal compound such as oxides, nitrides, carbides and borides, preferably from the group comprising alumina, titania, silica, stabilised zirconia, silicon nitride, boron nitride, silicon carbide, tungsten carbide, titanium borides and zirconium boride.

3. A die coating according to claim 1, said ceramic powder being selected from at least one mineral compound such as clay minerals, hard rock ore and heavy mineral sands such as those of ilmenite, rutile and/or zircon.

4. A die coating according to claim 3, said ceramics powder being obtained from scoria or pumice.

5. A die coating according to any preceding claim, said organic polymer powder being formed from a thermoplastic material, such as polystyrene, styrene-acrylonitrile, polymethacrylates, polyesters, polyamides, polyamide-imides and PTFE.

6. A die coating according to any preceding claim, each of said ceramic and polymer powders being of relatively narrow size spectrum.

7. A die coating according to claim 6, said ceramic and polymer particles being of particle sizes not more than about 60 μm and not less than about 1 μm in the case of said ceramic powder and not less than about 5 μm in the case of the polymer powder.

8. A process for providing a die coating on the surface of a mould or die component, wherein an initial coating of organic polymer material and ceramic material is formed on the surface by co-deposition of powders of the materials by a thermal spraying procedure, and the initial coating is heated so as to

remove the polymer material and leave a porous coating of the ceramic material.

9. A process according to claim 8, said polymer material being heated for removal by combustion and/or decomposition.

10. A process according to claim 8 or 9, said thermal spraying procedure being either flame spraying, plasma spraying or electric arc spraying.

11. A process according to any one of claims 8 to 10, wherein a substantially uniform die coat is provided over all surfaces of the mould or die components, which define a die cavity.

12. A process according to claim 11, said coating having a thickness of from about 250 to 400 μm.

13. A process according to claim 12, said coating having a thickness of from about 300 to about 400 μm.

14. A mould or die component having a surface for contact by molten metal in low pressure or gravity die casting, said surface being coated fully, or in a section or sections thereof, by a die coating according to any one of claims 1 to 7.

15. A mould or die component having a surface for contact by molten metal in low pressure or gravity die casting, said surface being coated in a section or sections thereof with a non-porous ceramic die coating and in another section or sections thereof, with a die coating according to any one of claims 1 to 7.

16. A metal mould or die component having a surface for contact by molten metal in low pressure or gravity die casting, said surface being coated fully, or in a section or sections thereof, by alternating layers of a non-porous ceramic die coating and a die coating according to any one of claims 1 to 7.

17. A die coating material for use in the process of any one of claims 8 to 13, said material being formed from a powder of a ceramic material and a powder of an organic polymer material.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. ^{7}: B22C 9/06, 9/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B22C 9/06, 9/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC AS ABOVE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Derwent: B22C 9/- and (mould+ or mold+) and (coat+ or layer+) and (ceramic+ or oxid+ or nitrid+ or borid+ or alumina or titania or silica or zircon or clay+ or ilmenit+ or rutil+ or scoria or pumic+) and (polymer+ or +plastic+ or poly+ or PFTE)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5277831 A (HANANO) 11 January 1994 See col. 1 line 55 to col. 3 line 32	1-17
A	DE 4313164 C1 (FREIBERGER NE-METALL GMBH) 9 June 1994 See whole document	1-17
A	EP 121929 A (SINTO KOGIO, LTD) 17 October 1984 See page 5 line 21 to page 7 line 15.	1-17

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:
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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 444394 A (SUGITANI KINZOKU KOGYU KK) 4 September 1991 See abstract	1-17
A	EP 191008 A (AB VOLVO) 13 August 1986 See abstract	1-17

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU00/00239

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	277831/5	CA	2041503	DE	4116260	GB	2253408
		JP	4279244	US	5277831		
DE	313164/4	EP	679462				
EP	121929	AU	26640/84	BR	8401651	CA	1266159
		IN	160636	JP	60006242	MX	161282
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END OF ANNEX